AEC-NASA TECH BRIEF

Transplutonium Elements Processed from Rock Debris of Underground Detonations

The problem:

To develop a processing method for isolating in high yield minute quantities of the transplutonium elements from gross constituents of rock and from fission products after a nuclear detonation. Underground nuclear detonations create isotopes of the transplutonium elements that are not readily produced in high-flux reactors. The explosions, however, distribute the transplutonium elements and fission products throughout large amounts of fused rock. Samples are obtained by drilling to appropriate depths and sorting the borings according to gamma activity. Those with the highest activities are processed and analyzed.

The quantities of transplutonium elements present in a sample are extremely minute. A minimum expenditure of time is available for processing because of the decay of short-lived isotopes. Also because of the high gamma activity of the rock debris, the initial processing of large quantities of rock must be performed in a high-level cave by remote control, complicating the process.

The solution:

A six-step chemical processing technique, using a liquid–liquid extraction, which can extract minute quantities of certain transplutonium elements found in rock debris following a nuclear detonation. The process can isolate in high yield less than one part of transplutonium element to 10^{12} parts of rock.

Small-scale experiments, where known quantities of Pu-239, Cm-242 and Cf-253 were added to the rock samples, produced recoveries in the range of 90–95%. Recoveries of plutonium and the transplutonium elements on a kilogram scale are estimated to be at least this good. To get a sample through the critical steps of the chemical process takes only 26 to 32 hours.

How it's done:

The chemical processing procedure developed consists of dissolution of rock, feed preparation, liquid–liquid extraction, final purification of the transplutonium elements, final purification of plutonium, and separation of the individual transplutonium elements.

The 1-kg. rock samples are essentially aluminum silicates containing small quantities of calcium, iron, and magnesium. The SiO_2 and Al_2O_3 contents are 60 to 70% and 10 to 20%, respectively. The CaO, Fe_2O_3, and MgO are all in the 0 to 5% range.

The pulverized rock is extremely reactive towards conc(28M) HF, so this acid affords an easy method of removing the silica. The gross cationic constituents, as well as the small quantities of transuranium and lanthanide ions, are left in a water-insoluble fluoride residue. The fluoride residue is converted into a concentrated chloride or nitrate salt solution by metathesis and acid-dissolution steps. This rapidly dissolves all the cations from the rock, except those soluble in HF, e.g., Zr, Hf, Nb, Ta, Mo, and W.

At this stage, an organic extractant is selected to remove transplutonium (III) and plutonium (IV) ions from the resultant Al, Ca, Mg, and Fe solution. Based on a recent study, a high-molecular-weight quaternary ammonium compound, Aliquot-336 nitrate, was selected as the extractant. High K_d values can be obtained for Am(III), Cm(III), Cf(III) and Es(III) by using a 0.4F xylene solution of the extractant and Li, Mg, Ca, and Al nitrate solutions in the range of 4 to 8N NO_3^- and $<0.1M H^+$. In addition, separation factors between transplutonium (III) ions and Li, Mg, Ca, and Fe(III) are greater than 10^3. Concentrated $LiNO_3$

(continued overleaf)

solution is an effective scrubbing agent for additional decontamination. Pu(IV) and La(III) ions are also highly extracted by Aliquot-336 nitrate, whereas certain fission products such as Cs, Sr, Zr, and Nb are not. The transplutonium(III) and La(III) ions are easily stripped from the amine with $2MNO_3$, while Pu(IV) remains in the organic phase. Adjusting the organic to aqueous phase ratios to <1 during the feed equilibration, and to >1 during the stripping equilibration, results in considerable concentration of transplutonium and lanthanide elements. Pu(IV) is stripped from the organic phase with $HC10_4$ or $Fe(SO_3NH_2)_2$.

At this stage, the transplutonium and lanthanide elements are highly decontaminated from gross constituents, such as Al, Ca, Mg, and Fe and a majority of the fission products. Final purification steps involve well-known ratiochemical techniques.

The main feature of this approach is the liquid–liquid extraction scheme. Although the extraction step is simple in concept, its success in actual processing of rock depends upon two conditions: first, the selection of the proper $[NO_3^-]$ and $[H^+]$ in the feed and the proper amine concentration in the organic phase to obtain the desired recovery of transplutonium elements; and second, the removal of colloidal and soluble silicic acid from the feed solution to prevent emulsion and interfacial precipitate formation.

The following conditions were selected:

Aqueous feed: ~7.5 nitrate ion, ~0.05N hydrogen

Organic phase: 04F Aliquot-336 nitrate in xylene

Phase Ratio (O/A): 0.5

Using these conditions, >99% of the transplutonium (III) ions can be extracted into the organic phase by two-batch equilibrations of the feed solution.

The silicic acid is removed by digesting the solution to dehydrate the majority of the acid. The remaining soluble silicic acid is precipitated by adding gelatin solution. This technique completely eliminates emulsion and interfacial precipitate formation.

Notes:

1. Complete details of the process and equipment used are published in "The Processing of Rock Debris for Transplutonium Elements Produced by Underground Nuclear Detonations," ANL-7134, February, 1966, Argonne National Laboratory, Argonne, Illinois. This report is available from the Clearinghouse for Federal Scientific and Technical Information, Springfield, Va. 22151; Price: $3.00 (microfiche $0.65).
2. This process may find application in the extraction of other heavy metals from low grade ores.
3. Inquiries concerning this report may be directed to:

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Patent status:

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